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METHOD OF MAKING A CONTAINER

Berthold C. Weber, Dayton, Ohio, assignor to the United States of America as represented by the Secretary of the Air Force

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The invention described herein may be manufactured and used by and for the Government for governmental purposes, without the payment to me of any royalties thereon.

As a background for imparting a clear understanding of the present invention as claimed, reference is made to the Berthold C. Weber and Phillip S. Hessinger application Serial No. 369,259, filed July 20, 1953, for patent on a Container Material and Melting Technique for Melting Reactive Metals and to the divided out Berthold C. Weber application Serial No. 434,092, filed June 2, 1954, for patent on an Oxygen Deficient Zirconia Container, both now abandoned, and with the Berthold C. Weber application Serial No. 797,309, filed March 4, 1959, for Refractory Material and Process, now U.S. Patent No. 3,049,432. The present application is a continuation-in-part of these earlier applications and has resulted from the summation of experimental work done by Dr. Berthold C. Weber on the same subject matter during the intervening time period. This application is copending with the above application Serial No. 797,309. Further study of the materials described in the earlier applications and the mechanism of their synthesis have revealed important improvements in both the materials and the methods here of interest.

This invention relates to a container for the metals titanium, zirconium, hafnium and thorium and the like, in the Group IVA, such as of the periodic chart of the elements in Metals Handbook published in 1948 by The American Society for Metals, 7301 Euclid Avenue, Cleveland 3, Ohio, at page 22, and more particularly to an improved container made of zirconia and these metals and the containers used for melting and casting these metals.

A brief summary of the invention follows, indicating its nature and substance together with a statement of the objects of the invention commensurate and consistent with the invention as claimed and also setting out the exact nature, the operation and the essence of the invention complete with proportions and techniques that are necessary with its use. The purpose of the invention also is stipulated. The presentation is adequate for any person who is skilled in the art and science to which the invention pertains to use it without involving extensive experimentation. The best mode of carrying out the invention is presented by the citing of specific operative examples inclusive of the preparation and the use of at least one example of the invention.

The objects of the present invention are to provide new and superior compositions for the fabrication of crucibles, molds and the like used in melting metals, such as those in Group IVA of the Periodic System, without contaminating the melt or the castings taken from the molds; the provision of melting crucibles, casting molds and the like that have good thermal shock resistance; the provision of a metal modified zirconia material; the process in the metallurgy of titanium of providing an improved container for liquid titanium that is chemically inert thereto and that replaces the earlier water cooled copper crucible, and that is suitable for inductance heating; the making of alloys of accurate compositions of the metals here of interest; and the like.

The metal titanium is of increasing importance because it is a lightweight, strong, corrosion resistant and

ductile metal of high melting point. It fills a gap between aluminum alloys and stainless steel in its density, modulus of elasticity, and strength at solid state temperatures. The metal titanium is particularly favored for aircraft use because of its high strength to weight ratio; its outstanding sea water and marine atmosphere corrosion resistance, which exceeds that of austenitic stainless steel and is equal to that of platinum and comparable material.

The desirable metallic properties of titanium are destroyed by embrittlement in the presence of interstitial impurities such as oxygen, nitrogen and hydrogen. Hydrogen can be removed from titanium by a vacuum treatment. When titanium has dissolved oxygen and nitrogen, the oxygen and nitrogen cannot be removed from the titanium by any known method.

The melting of titanium without contamination has been a major problem in its fabrication. Every known crucible material is attacked to some degree by molten titanium. In "skull melting," using the arc melting technique, a layer of titanium may be frozen against a refractory crucible to serve as an inside wall in contact with the molten titanium. Another method used with the arc melting technique employs water cooled copper crucibles with water close to the molten metal, which introduces an explosion hazard. An induction melting method is preferred. The ceramic crucible that is contemplated herein does not require cooling and has material advantages over earlier crucibles that are set forth more extensively hereinafter.

Studies of the systems Ti-O, Zr-O and some phases of the ternary system Ti-Zr-O led to the concentration on zirconia as the base constituent for crucible material. Zirconia appeared to be the most promising refractory from its free energy of formation and heat of formation. These studies led to an oxygen deficient zirconia material that is made stable thermally by reacting zirconia with titanium metal powder as a novel refractory material. Zirconium has a higher affinity for oxygen than titanium has and can take oxygen away from titanium oxide. X-ray diffraction analysis indicates that when TiO_2 plus Zr are reacted the end products are monoclinic zirconia and an expanded titanium lattice. It is concluded that zirconium reduces titania and that zirconia is not reduced by titanium. The chemical reduction does not involve or concern the substitution of a zirconium atom by a titanium atom in the ZrO_2 lattice.

Zirconia is one of the most refractory of the oxides. The melting point of zirconia is 2680±20° C, which is about 4850° F. Pure zirconia possesses monoclinic symmetry at room temperature of about 20° C. to 25° C.; and at about 1000° C. it transforms reversibly to tetragonal crystal modification, accompanied by a large change in thermal expansion. Pure zirconia products crack badly on heating and cooling.

The new approach to thermally stabilizing zirconia which is chemically inert to attack by molten titanium has evolved from an investigation of the systems ZrO_2-TiO and ZrO_2-Ti, from which specially promising results were obtained from the system ZrO_2-Ti.

Crack-free and thermal shock resistant crucible specimens, that were black in color throughout, were obtained when mixtures of titanium metal powder and pure zirconia powder were sintered in a vacuum at temperatures that range from 1760° to 1870° C. and above, or 3200° to 3400° F. and above. An experimentally successful crucible is made of ZrO_2 with a fifteen atomic percent titanium addition. On firing this material a substitutional solid solution of titanium in zirconia having a defect structure due to an oxygen deficiency is formed. Its inertness to molten titanium is believed to be accounted for by the low oxygen availability of the material.

Container fabrication

The batch preparation for making a container such as a crucible consists illustratively of the weighing out of 93.5% ZrO_2 and 6.45% Ti metal powder. The metal powder is of the highest purity available, such as titanium in excess of 99% by weight of elemental titanium. The zirconia raw material is in excess of 98.9% ZrO_2. An illustrative available fineness of the powder is −325 mesh. Crucible shapes are made by conventional methods of pressing, jiggering or slip casting. For pressing, the batch is suspended in methyl alcohol, mixed by short ball milling, pressed in a mold to shape the powdered mix, the shape is air dried at room temperature, fired in a vacuum, and then the shape is cooled in the vacuum to room temperature.

The preparation of a casting slip is accomplished illustratively by short ball milling the batch of 93.5% ZrO_2 and 6.45% Ti powders mixed with one normal hydrochloric acid as deflocculent. The resultant slurry of creamy consistency, is then freed of air bubbles using a water pump and is checked for pH, grain size and viscosity. The slip is then cast in plaster of Paris molds, using drain casting techniques common to the porcelain and clay industry. The cast shape releases easily from the mold after a short drying period at room temperature. The cast shape is removed from the mold, completely air dried and is heated to 100° C. for a short period.

The dried cast shape, such as a crucible, is then fired in a vacuum of at least 5×10^{-4} mm. of mercury. The composition has a wide sintering range of illustratively from 1760 to 1870° C. and above, or 3200 to 3400° F. and above. The sintered piece is held at the sinter temperature and soaked for one hour and is then cooled to room temperature before braking the vacuum. The fired pieces are black throughout. The material is hard, strong and crack-free. It has a bulk density of 5.5 g./cm.^{3} and a true specific gravity of 5.7 g./cm^3. It has substantially no porosity, its water absorption being about 0.1%. The total shrinkage is about 20% for slip cast and 15% for pressed crucibles.

The zirconia containing 15 atomic percent of Ti material has an excellent thermal shock resistance. Experimental crucibles were cycled rapidly several times from room temperature to 1900° C. or 3450° F. at 10 minute periods, with no observable cracks.

X-ray and microscopic studies of the material have been made without completely clarifying how zirconia and titanium combine. The room temperature X-ray analysis of the fired ZrO_2 containing 15 atomic percent of Ti produces a very weak, scarcely detectable expanded titanium pattern. The principal phase is monoclinic zirconia. The weak titanium pattern, dark color of the reaction product, and its high thermal shock resistance, suggests a solid solution of titanium in zirconia, but a noticeable shift in the lattice constant of zirconia is not observed. Elevated temperature X-ray studies indicate the usual monoclinic to tetragonal inversion of zirconia.

A possible explanation for the inertness of the 15 atomic percent titanium in zirconia composition to molten titanium is that 15 atomic percent of titanium represents the saturation point for Ti solution in ZrO_2 at the elevated temperature, which is analogous to 15 atomic percent Zr solubility in ZrO_2 as described in the literature. As the total amount of Ti which can dissolve in ZrO_2 at the melting point of Ti is already in the crucible composition, the possibility of attack is thus reduced. Atomic percent is defined at page 83 of Hackh's Chemical Dictionary by Julius Grant, 1946 printing, published by The Blakiston Company, Philadelphia, Pa. Zirconia-titanium solid solution at room temperature is of black color and is free from cracks. By sintering titanium in a vacuum, the titanium forms a substitutional solid solution with zirconia resulting in an oxygen deficient zirconia lattice. On cooling the solution of titanium in zirconia some of the tatanium comes out of solution. The thermal shock resistance of the material is explained by the stress relieving nature of this metal component, in addition to an increased thermal conductivity and the high strength of the material.

Melting procedure

In the melting of titanium in crucibles made of this titanium saturated zirconia material, the evaluation of the melts by Vickers hardness determinations demonstrate that there is no significant increase in hardness when the melts are not superseated. The three factors which mainly influence the successful use of this crucible material as a container for molten titanium are the melting temperature, the soaking time, and the atmosphere purity.

Undue overheating of the melt must be avoided so as not to reach a final equilibrium condition between the melt and the crucible material, as is commonly required in the ceramics field to obtain optimal properties. The ceramic processes are processes of arrested reactions, in comparison with the metals processes wherein melts commonly are overheated to lower the metal's viscosities for casting operations.

In the use of resistance heating the metal charge is melted by heat transmitted through the crucible wall, which means the crucible is at a higher temperature than the charge. The reactivity of molten titanium with the crucible material increases exponentially with temperature and hence superheating increases the reaction rate many fold. To minimize any reaction between the melt and the container material, the recommended heating schedule is to balance the crucible melt temperature below the metal melting point and then overheat for as short a time as possible and only as high as is actually required to obtain the proper metal viscosity condition for casting.

The purity of the furnace atmosphere that is essential for successful titanium melting is not as much of a problem on a laboratory scale as it is in industrial practice, as will be appreciated by designers of furnaces.

Induction-type melting with the possibility of reduced melting time, provides more favorable conditions than does resistance heated furnaces. If a suscepter is required, molybdenum or tungsten are preferred to graphite. The titanium metal charge itself may be used as the suscepter, in which case a suitable backing material that is stable both in a vacuum and in contact with titanium vapor must be employed, such as prefired material of the crucible composition in granular form. The fact that zirconia becomes an electrical conductor above 1000° C. does not appear to be a problem because of the higher conductivity of the metal.

For the melting of titanium the charged crucible is placed in a furnace designed for either vacuum or neutral atmosphere firing. Both the crucible and the charge are first degassed by evacuating the furnace to about 2×10^{-4} mm. mercury and heating in vacuo to approximately 1000° C. Soaking at this temperature for 15 minutes is adequate for the removal of practically all of the air that is absorbed in both the charge and the crucible.

Following the degassing of the furnace and its charge, purified helium is introduced into the furnace and the furnace temperature is gradually increased until the titanium charge is melted. After the complete melting of the titanium is observed, the power into the furnace is shut off and the helium atmosphere is maintained until the furnace and its charge have cooled to room temperature.

It is of utmost importance that a satisfactory furnace atmosphere is maintained, with the vacuum above 5×10^{-4} mm. of mercury during the degassing stage of the firing and with an extremely pure helium gas atmosphere during the later stage of the melting operation. Leakage in the helium system can best be avoided by using an all glass purification train. The helium, preferably of grade

A, is passed through a liquid nitrogen trap, a desiccant such as anhydrous calcium chloride or the like, and a 1000° C. getter furnace illustratively using a getter alloy of 65% Zr and 35% Ti is preferred to titanium sponge for removing the last traces of oxygen from the helium.

While the crucible material composed of ZrO_2 with an addition of Ti was successfully used to melt titanium without contamination, the basic principle derived from the research which led to the invention can be applied also to synthesize container materials for melting other reactive metals, not only zirconium, hafnium and thorium, which are sister or analogous metals to titanium and zirconium according to the Mendeljeff classification of elements, belong to Group IVA of the Periodic Table, but also chromium and other refractory metals having a melting point below approximately 2500° C. or 4530° F. In each case the individual metal to be melted is added to zirconia and containers formed from these compositions are fired in vacuo to result in an oxygen deficient metal modified zirconia material. The name "metal modified oxide" (MMO) has been coined for this new class of materials.

Successful melting experiments have already been conducted, in addition to titanium, with zirconium and chromium in containers composed of ZrO_2 plus 15 atomic percent of Zr and ZrO_2 plus 15 atomic percent of Cr respectively. In the case of chromium-modified-zirconia it is necessary to change the firing conditions because of the volatility of chromium in vacuo. These crucibles of chromium-modified-zirconia, therefore, have to be fired in a helium or argon atmosphere at atmospheric pressure.

The process and the products that are disclosed herein

are submitted as experimentally confirmed improvements in the melting and in the casting of the Group IVA metals and similar highly reactive metals of high melting points, such as Cr, Th and the like, and comparable modifications may be made therein without departing from the spirit and the scope of this invention as defined in the claim appended hereto.

I claim:

The method of making a container for molten titanium comprising forming a mixture of 93.5 percent ZrO_2 powder and 6.45 percent Ti powder, adding methyl alchohol to the powder mixture to form a suspension, casting the suspension into a desired shape, air drying the shape, firing the dried shape in a vacuum at a temperature in the range from about 1760° C. to about 1870° C. and cooling the fired shape in the vacuum.

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TOBIAS E. LEVOW, *Primary Examiner.*

JOHN H. MACK, *Examiner.*